## The Formation Age of Comets: Predicted Physical and Chemical Trends

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The chemical composition of a comet has always been considered to be a function of where it formed in the nebula. We suggest that the most important factor in determining a comet's chemistry might actually be when it formed. We present specific predictions of correlations between the dust and volatile components to test our hypothesis.

It is well established that the Falling Evaporative Bodies (FEBs) responsible for anomalous red-shifted UV extinction in Herbig Ae and Be stars are actually star-grazing comets<sup>4,5</sup> undergoing rapid loss of both gas and dust close to the central star. FEBs have been reported for Herbig Ae and Be systems of all ages, but are most frequent in younger systems. Since the first observations of the disk around Beta Pictoris<sup>6</sup> (a relatively old protostellar A star) it has been recognized that such disks are unstable to dust loss via radiative forces and must be replenished on a more-or-less continuous basis from larger bodies such as comets. Knacke et al. demonstrated that the mid-infrared spectrum of the grains in the disk of Beta Pictoris is consistent with the spectrum of dust grains observed in Comet Halley<sup>8,9</sup> and attributed by the authors of the latter papers to crystalline olivine. Sitko et al. 10 reviewed the trends observed in the mid-IR spectra of Herbig Ae and Be stars as a function of age for stars without detectable companions. They demonstrated that this spectrum evolves smoothly from that of amorphous astronomical silicate<sup>11</sup> to a spectrum consistent with crystalline olivine. Although these spectral changes could potentially result from exposure of initially amorphous grains to x-rays from the young star, a more likely explanation is that these changes result from thermal processing in the nebula.

The rate of spectral change in initially amorphous magnesium silicate smokes as a function of temperature has been measured by Hallenbeck et al. who determined that this rate was extremely sensitive to the annealing temperature. More recent studies allow one to predict the mid-infrared spectrum of annealing magnesium silicate dust if its time-temperature history can be hypothesized<sup>2</sup>. Based on this work, the time required for initially amorphous astronomical silicate grains to thermally anneal to crystalline olivine at 1000 K is on the order of a few hundred days. This same transition occurs in less than two hours at a temperature of 1050 K, but requires at least 100 years

at 950 K, and nearly 4 billion years at 850 K. Alternatively, if isolated presolar silicates become too hot (e.g. T > 1400 K) they will evaporate. Upon cooling, this vapor will recondense to form amorphous silicates, not crystalline grains. Therefore, the production of significant quantities of crystalline olivine from initially amorphous interstellar materials requires dust processing at moderate temperatures (T~1000 K), probably near 1 AU or so<sup>3</sup>, followed by transport of the newly created crystalline olivine grains to beyond the nebular snowline for incorporation into the next generation of embryonic cometesimals.

One would expect comets and cometesimals to form throughout the history of a protostellar disk. The cometesimals that formed earliest must of necessity contain nearly pure interstellar grains and ices. These comets would be dominated by amorphous silicates, CO, CO2, N2 and water ice, e.g., see Gerakines et al. 12. These materials would dominate the composition of the FEBs observed in very young Herbig Ae and Be stars, as these comets replenish the dust disks around such stars. Cometesimals formed later could contain more highly processed dust, provided that some mechanism exists to transport this annealed dust component to beyond the snowline. Prinn<sup>13</sup> and Stevenson<sup>14</sup> have previously discussed the likelihood of outward mixing in a nebular environment due to nonlinear momentum terms often neglected in nebular models. The observation that the dust in disks around older Herbig Ae and Be stars (without companions) appears to have been annealed in a manner consistent with the observed spectral evolution of the amorphous magnesium silicates reported by Hallenbeck et al. 1 supports the hypothesis that such a transport mechanism exists. Dust released by comets in older Herbig Ae and Be systems contains more highly processed materials than the dust released just as such systems begin to break out of their dusty cocoons. These grains most likely formed via thermal annealing of initially amorphous astronomical silicate grains. If individual dust grains are transported from the inner nebula to beyond the snowline, then it makes sense to assume that some portion of the gas in the inner nebula also makes this journey. Such transport would have very interesting consequences for cometary chemistry.

Models of cometary chemistry<sup>15, 16</sup> have always had difficulty explaining the observed ratio of interstellar molecules – such as CO, N<sub>2</sub>, etc. – to molecules produced in the solar nebula. Formation of these more complex materials, e.g., hydrocarbons, ammonia, etc., requires higher pressures and temperatures than those found in nebular models for regions beyond the orbit of Jupiter or Saturn. A possible way around this dilemma has been to postulate the existence, and subsequent breakup, of Giant-Gaseous Protoplanets that could provide the thermodynamic environment required to synthesize more complex molecules observed in comets from interstellar ices that barely even vaporize in the outer regions of the Solar Nebula. Continuous cycling of just a small fraction of nebular gas and grains from the higher pressure, higher temperature inner nebula to beyond the nebular snowline obviates the need for Giant-Gaseous Protoplanets as an explanation for the more complex chemistry of comets. However, operation of this transport mechanism throughout the history of the nebula would predict some very specific correlations between the chemistry of comets and the mid-infrared spectra of their dust.

As noted previously, comets formed early in the history of the Solar Nebula will consist almost exclusively of amorphous silicates and unaltered interstellar ices. The probability that many such comets survive to the present era cannot be adequately addressed here. However, we can conclude that cometesimals formed at later times will contain an increasing fraction of annealed silicate dust together with an increased ratio of hydrocarbons to CO or CO2, and an increased ratio of ammonia and more complex amines and amides to molecular N2. As these cometesimals accrete into comets, the average comet formed late in nebular history will contain more hydrocarbons, ammonia and annealed dust than one formed earlier. The time-dependent nature of the dust and gas accreted into comets might easily obscure less significant differences in cometary chemistry - such as the potential distinction between comets accreted in the Jupiter-Saturn region from those accreted near Uranus-Neptune. One must also be cognizant of the statistical nature of this indicator: dust annealed at a wide variety of temperatures could find its way to the same comet. Thus, a minor component of very-wellannealed dust in one comet would not necessarily imply the same chemistry found in a comet containing mostly moderately annealed dust. As a general rule, the chemistry of the comet would be correlated with the bulk of the dust. For example, a comet containing a minor component of very well annealed dust and a major fraction of amorphous dust most likely formed -

on average - before a comet containing only moderately annealed dust. Whereas the chemistry of the former comet would be rich in CO, CO<sub>2</sub> and N<sub>2</sub>, the latter comet should contain an abundance of hydrocarbons, ammonia and other essential prebiotic compounds.

We predict that the fraction of crystalline cometary dust is correlated to the ratios of hydrocarbons to CO/CO<sub>2</sub> and ammonia/amines/amides to N<sub>2</sub> and we challenge the observational community to test this hypothesis. Such observations can simultaneously corroborate the existence of a transport mechanism between the inner and outer regions of protoplanetary nebulae based on our predictions concerning cometary chemistry and establish a method to determine the formation age of comets. An ability to sequence comets according to their relative ages could be a useful tool in understanding a number of events in the primitive Solar Nebula and would provide an interesting discriminator in choosing targets for space flight missions.

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